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Review

Recent progress in 2D materials for flexible supercapacitors[†]

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[†]Dedicated to Professor Jin-Pei Cheng on the Occasion of His 70th Birthday.

Abstract

High performance supercapacitors coupled with mechanical flexibility are needed to drive flexible and wearable electronics that have anesthetic appeal and multi-functionality. Two dimensional (2D) materials have attracted attention owing to their unique physicochemical and electrochemical properties, in addition to their ability to form hetero-structures with other

nanomaterials further improving mechanical and electrochemical properties. After a brief introduction of supercapacitors and 2D materials, recent progress on flexible supercapacitors using 2D materials is reviewed. Here we provide insights into the structure-property relationships of flexible electrodes, in particular free-standing films. We also present our perspectives on the development of flexible supercapacitors.

Key Words: 2D materials; Flexible supercapacitors; Graphene; Molybdenum disulfide; MXenes

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1. Introduction

Flexible or wearable energy storage devices with high performance are highly desirable to drive flexible/wearable electronics and Internet of Things (IoT), in particular those multifunctional electronic devices that can monitor, sense and communicate at the same time [1–9]. The lithium ion battery (LIBs) is currently the best performing battery for applications in portable devices, since it has the highest energy per unit of weight and volume, long service life, and wide operating temperature in comparison to other established energy storage systems [10–13]. The

research on flexible LIBs has attracted widespread attention from both the academic and industry [14, 15]. The electrode materials used have spanned from inorganic compounds [16–18] to sustainable organic conductors that may be derived from the biomass [19–22]. There exist some excellent reviews on design and configuration of flexible or even stretchable energy storage devices [23–25] including the novel textile-based [26], paper-based [27, 28] and cable-type [29].

Being an important member of energy storage family, supercapacitors can store and deliver energy at a very fast rate. They possess merits of high power density, fast charging-discharging ability, extremely long cycling life, and ability to bridge the power/energy gap between conventional capacitors and batteries/fuel cells [30–33]. Supercapacitor is also named as electrochemical capacitor or ultracapacitor. According to the energy storage mechanism, supercapacitors are generally classified into electrochemical double layer capacitors (EDLCs) and pseudocapacitors [34, 35]. EDLCs physically store charges via reversible adsorption/desorption of ions at the electrode/electrolyte interface. Since non-faradaic (chemical redox) reactions are involved, EDLCs have extremely long cycle life but low energy densities. Pseudocapacitors involve fast reversible Faradaic redox reactions at the surface of electrode materials, which can provide higher energy density at the price of short cycle life and low rate capability. Hybrid supercapacitors (HSCs) use two types of materials with different fundamental working principles, where non-faradaic charge-discharge process occurs on the capacitive carbon electrode coupled with a surface-confined redox reaction on the negative electrode [36,37]. This combines the merits of EDLCs and pseudocapacitors affording higher energy density while keeping good cycling stability.

Flexible supercapacitors are of great interest owing to their high power density, high flexibility, space efficiency, light weight and ease of handling [23, 25, 29]. They usually consist of thin-film electrode materials with high flexibility in planar or fiber shape with or without mechanical support (soft-matter substrates). The strong integration of active material with flexible substrate enables mechanical robustness and flexibility. Free-standing films/papers or fibers can be used directly as electrodes without addition of conducting additives and insulating binders, providing high gravimetric and volumetric performance. They can also be easily engineered into any desired shapes or structures [38,39]. The widely used nanostructured materials for high performance supercapacitors include hierarchical porous carbons, carbon nanotubes (CNTs), and hollow structured metal oxides/sulfides [40-45].

Two-dimensional (2D) nanomaterials have attracted great interest in recent times due to their extraordinary physicochemical properties. They belong to a unique material family with a thickness of a single or several atomic layers [46, 47]. This unique ultra-thin nature gives large specific area for charge storage. Also, the simple 2D sheet structure with large aspect ratio endows them with direct incorporation with other nanomaterials creating new compositions for higher performance; and a self-assembly process for 3D structures with high mechanical integrity and flexibility originating from the large overlapping areas [48, 49]. All these properties make them promising candidates for applications in flexible supercapacitors. However, those 2D nanosheets tend to restack and aggregate owing to their large aspect ratio, the strong π - π interaction and van der Waals forces between them. This leads to severe shrinkage of the accessible surface area, limiting their electrochemical performance. Creating new compositions

with other nanomaterials and/or forming three dimensional porous structures are effective approaches to fully utilize their potential to achieve high charge storage capability.

In this review we will discuss graphene and its inorganic analogues transition metal dichalcogenides (TMDs) and Mxenes (e.g. transition metal carbides, carbonitrides, nitrides) that have been demonstrated the application in flexible supercapacitors; their typical fabrication methods will be presented first.

2. Fabrication methods of 2D materials

Ultrathin 2D nanomaterials can be obtained from exfoliation of layered bulk crystals, which have strong intraplane covalent bonding but weak interplane van der Waals interactions. Reliable methods have been pursued for fabrication of 2D nanomaterials with optimal physicochemical properties along with suitable structures. Generally, they can be divided into two categories: top-down and bottom-up approaches [50–52].

The stacked layers in bulk crystals can be exfoliated to single- or few-layer ultrathin 2D nanosheets by the top-down approaches, mainly including mechanical exfoliation [53–57], liquid exfoliation [58–62] and ion/molecules-intercalation assisted exfoliation strategy [63–67] (Fig. 1). Mechanical exfoliation strategy is commonly referred to as the Scotch-tape method, whereby a few layers or even a single layer of 2D nanomaterial can be extracted from the bulk crystals surface [53, 68]. Since no chemical reactions are involved, the obtained 2D nanomaterials still remain their pristine structure and intrinsic properties that are suitable for the structure-property

relationship investigation. However, it is a time-consuming method with quite low production yield that results in limitations in practical applications.

Liquid exfoliation [69, 70] and ion/molecule-intercalation assisted exfoliation [71–74] are two common strategies used to produce 2D nanosheets in large quantity. The liquid exfoliation process is carried out under an external stimulation forces: ultrasonication in solvents. A good matching of surface tension between solvents and produced nanosheets is critical for efficient exfoliation [58,59]. N-methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF) are two commonly used solvents. This method also suffers from low yield and less control over the dimension of nanosheets. The ion/molecule-intercalation assisted exfoliation refers to intercalation of ions or molecules into the interlayer spacing of layered bulk crystals to enlarge interlayer distances and weaken the van de Waals interaction between layers. Single- or few-layer nanosheets can be easily exfoliated from these ion/molecules intercalated bulk crystals under ultrasonication in solvents. Commonly used intercalators include organometallic compounds such as butyllithium [67, 75], or small molecules such as H₂O [66, 74] or NH₃ [76]. Intercalating ions (e.g. Li⁺ and H⁺) into layered compounds can also be achieved via electrochemical routes, and the amount of intercalated ion can be monitored and controlled [65, 72, 73]. For the production of graphene nanosheets via liquid-phase exfoliation, a graphite oxide precursor that may be synthesized by Hummers method [77], is commonly used. Generally, bulk graphite are first oxidized into graphite oxide by strong oxidizing agents, and then exfoliated into graphene oxide (GO) sheets under ultrasonication [78]. The produced GO with abundant oxygen-containing functional groups is an insulating material. Removing the functional groups to form

graphene (e.g. reduced graphene oxide, rGO) can be achieved via chemical reduction [79], thermal annealing [80] or electrochemical reduction [81].

Fig. 1 Schematic illustration of the exfoliation process of 2D nanosheets from the layered bulk materials: (a) Scotch-tape method and (b) ultrasonication-assisted liquid-phase exfoliation process [50]; (c) ion/molecules-intercalation assisted exfoliation [52].

Bottom-up methods rely on direct synthesis of 2D nanomaterials using various precursors by chemical reactions route, mainly including chemical vapor deposition (CVD) [82–84] and wet-chemical synthesis [85]. The CVD method can produce highly crystalline 2D nanomaterials with flexible size and thickness on solid substrates. Various 2D nanomaterials have been synthesized using this method such as graphene [83, 86, 87], h-BN [88–90], and TMDs [91–96]. Its limitation lies in the fact that it involves complicated and expensive procedure which requires a high vacuum, high temperature and a specific solid substrate to support the growth of 2D

nanomaterials. Wet-chemical synthesis is another bottom-up method used to prepare 2D nanomaterials from precursors via chemical reactions in solution. It includes hydro/solvothermal synthesis, template synthesis, self-assembly of nanocrystal, and colloidal synthesis [97–102]. This method has been demonstrated to be effective for synthesis of numerous layer structured 2D nanomaterials including graphene (Fig. 2a) [97, 103, 104], TMDs [101, 105] and layered double hydroxides [106, 107]; non-layer structured 2D nanomaterials (i.e. metal [108, 109], metal oxides/hydroxides [99, 110], and non-layered metal chalcogenides (Fig. 2b) [111, 112]). Wet-chemical synthesis can be used to realize high reaction yield for mass production at relatively low cost. Moreover, the size, shape and morphology can be controlled by tuning reaction parameters.

Fig. 2 Schematic illustration of the wet-chemical synthesis of 2D nanosheets: (a) ordered mesoporous graphene nanosheets [104]; (b) single- and multilayer transition-metal sulfide nanosheets [112].

3. Free-standing graphene films for flexible supercapacitors

Graphene was experimentally discovered by Geim and co-workers in 2004 [53]. Its unique 2D planar carbon honeycomb structures can be considered as the basic building blocks for other 0D, 1D and 3D carbon materials (Fig. 3) [113]. Graphene possesses a very high theoretical specific surface area (SSA, $\sim 2630 \text{ m}^2 \text{ g}^{-1}$) [78], leading to a high theoretical electrochemical double layer capacitance of $\sim 550 \text{ F g}^{-1}$ [114]. Combining its excellent electronic conductivity and outstanding mechanical properties, graphene has been considered as promising electrode materials for flexible supercapacitors [114]. Over the past decade, tremendous efforts have been devoted in developing graphene-based flexible electrodes including free-standing film electrodes [115–117], substrate supported electrodes [118–121] and fiber electrodes [122–124]. There exist some excellent reviews on graphene-based flexible supercapacitors [114, 125–127]. In this review we mainly focus on free-standing graphene-based films with novel three-dimensional porous structures.

Fig. 3. 2D graphene as building blocks for other dimensional carbon materials [113].

Flexible, ultrathin and lightweight free-standing graphene films (or paper) are promising electrodes for flexible supercapacitors affording high gravimetric and volumetric capacitance since nonconductive binders and inert additives are eliminated. Using graphene oxide (GO) precursors, free-standing graphene films with a well-ordered layer structure can be easily fabricated through vacuum filtration [79, 128, 129]. However, graphene nanosheets are prone to restack during the fabrication process due to the strong π - π interaction and van der Waals forces between graphene nanosheets, limiting the available surface area and compromising electrochemical properties. Strategies to prevent the re-stacking of graphene nanosheets mainly include incorporation of nanomaterials as spacers [115, 116, 130–139] or the creation of 3D porous structures [117, 140–151] as discussed below.

3.1. Incorporation of nanomaterials between graphene nanosheets

3.1.1. Non-redox-active species

The 2D sheet structure and rich chemistry of graphene nanosheets enable the introduction of a variety of materials as spacers that can be either electrochemically inert [115, 116, 130–133] or redox-active species [134–139] to form graphene composites. Non-redox-active spacers include carbon materials [130, 131], polymers [132] and even solvent molecules [115, 116, 133]. For example, restacking of graphene sheets is alleviated by introduction of carbon black nanoparticles [130], and the obtained paper delivered a capacitance of 138 F g^{-1} at a scan rate of 10 mV s^{-1} in 6 M KOH with negligible capacitance loss over 2,000 cycles at 10 A g^{-1} . The presence of highly conductive CNTs in a graphene oxide (GO)/CNT hybrid film not only prevented the restacking of graphene nanosheets (Fig. 4a) but also allowed for effective electrochemical reduction of the GO, resulting in an excellent rate capacitance of 90 F g^{-1} at a current density of 100 A g^{-1} , compared to that 30 F g^{-1} at 30 A g^{-1} for graphene-only film [131].

The simple inert solvent molecules can also act as spacers. Yang et al. reported a chemically converted graphene film solvated with water molecules (SSG film), in which graphene sheets were well separated, displaying an open pore structure for easy access of electrolyte (Fig. 4b-d) [115]. This film showed a large specific capacitance up to 215.0 F g^{-1} at 0.1 A g^{-1} with an outstanding rate capacitance of 156.5 F g^{-1} at an ultrahigh current density of 1080 A g^{-1} . The packing density of this graphene film could be controlled by changing the ratio of volatile water and non-volatile liquids contained in this hydrogel [116]. The film with a high density of 1.33 mg cm^{-3} was obtained after removal of volatile solvent (Fig. 4e-g). It exhibited a high specific capacitance of 255.5 F cm^{-3} in 1 M H_2SO_4 and 261.3 F cm^{-3} in 1 M EMIMBF₄ at 0.1 A g^{-1} .

Fig. 4 (a) SEM image of a GO/CNT hybrid film [128]. (b) Photo of a flexible SSG films. Schematic (c) and SEM image (d) of the cross-section of a SSG film [115]. (e) Photo of a flexible EM-CCG film. (f, g) SEM cross-sectional images of EM-CCG films with a mass loading of 0.42 and 1.33 mg cm⁻³ [116].

3.1.2. Redox-active species

Non-redox-active spacers can benefit the structure construction, but hardly contribute additional capacitance. Redox-active spacers such as conducting polymers [134–137] and metal oxides [138, 139] can perform these two functions simultaneously. Conducting polymers are unique materials that possess the mechanical properties of polymers and electronic properties of metals or metal oxides [152]. They can be used as active materials alone or as one component in the composites for supercapacitors owing to their intrinsic characteristics such as high electrical

conductivity, interesting redox properties, soft “nature”, and easy processability [153–155]. Graphene/polyaniline (PANi) nanofiber composite films produced via vacuum filtration demonstrated a layer-by-layer structure, where the chemically synthesized PANi nanofibers were uniformly sandwiched between graphene layers (Fig. 5a,b) [134]. Such film exhibited a specific capacitance of 210 F g^{-1} at 0.3 A g^{-1} (Fig. 5c), and a capacitance retention rate of 94% when the current density was increased from 0.3 to 3 A g^{-1} . Similar results have also been demonstrated for graphene with incorporation of metal oxides. Layer structured graphene@Ni(OH)₂ hybrid films via filtration [139] (Fig. 5d, e) showed well enhanced gravimetric ($\sim 573 \text{ F g}^{-1}$) and volumetric ($\sim 655 \text{ F cm}^{-3}$) capacitances. The assembled device exhibited a consistent capacitive performance upon subject to a bending at different angles (Fig. 5f).

Fig. 5 (a) Photo of a flexible graphene/PANi nanofiber film; (b) Cross-sectional view of the film; (c) Charge/discharge curves of the supercapacitors using graphene/PANi nanofiber film (G-PNF₃₀), PANi nanofiber (PANI-NF), and chemically converted graphene (CCG) films at 0.3 A g^{-1} [134]; (d, e) SEM images of the cross-section of graphene@Ni(OH)₂ hybrid films; inset photo

shows the flexibility; (f) Cyclic voltammograms of the flexible supercapacitors measured at different curvatures of 0°, 90°, and 180° [139].

3.2. Creation of three dimensional (3D) porous architecture

Fabricating conductive graphene nanosheets into a 3D porous architecture is another commonly used strategy to improve the performance. The produced micro-, meso- or macroporous structures can effectively improve surface area, providing extra channels for rapid transport of charge carriers within conductive graphene frameworks. Such a 3D porous structure can be achieved through template-assisted [140–146] or template-free [117, 147–151] approaches.

3.2.1. Template-assisted assembly

Macroporous graphene films with pore size ranging from sub-micrometers to several micrometers are the mostly reported. Their architectures can be created in a controllable manner by using templates (hard templates and soft templates). The commonly used hard templates include polymer nanoparticles [140, 141], metal or metal oxide frameworks [142–144]. For example, using monodisperse polymethyl methacrylate (PMMA) spheres as a template, a PMMA/GO film with a sandwich structure was fabricated via filtration [140]. After removal of PMMA by a calcination process at 800 °C, a macroporous “bubble” graphene film was obtained (Fig. 6a, b). This film showed an excellent capacitance retention rate of 67.9% at scan rates from 3 to 1000 mV s⁻¹. Microchannel-network graphene foams could be produced by anchoring GO nanosheets onto a sacrificial alumina fiber blanket followed by removal of template [144]. The resulted foam demonstrated a high specific capacitance of 216 F g⁻¹ at 0.5 A g⁻¹.

It is interesting that a 3D porous structure can also be formed using soft templates such as liquid droplets [145, 146]. Lee et al. casted the polymer-grafted GO dispersion in benzene onto a SiO₂ substrate and exposed it in humid air flow [145]. During the endothermic evaporation of benzene, the condensation and close packing of water droplets at the organic solution surface created a macroporous structure (Fig. 6c, d). A tuneable pore size and numbers of porous layers can be controlled by changing the concentration of organic precursor dispersion and length of polymer chains grafted on the GO surface. This macroporous nitrogen-doped graphene electrode showed an improved specific capacitance of 103.2 F g⁻¹ in 1 M H₂SO₄.

Fig. 6 Schematic illustration of the fabrication process of macroporous bubble graphene film (a) [140] and macroporous carbon films (c) [145]; and SEM images respectively demonstrate their porous structures (b, d).

3.2.2. Template-free assembly

Since using templates commonly involves a costly or tedious process, the template-free fabrication method has attracted attention [117, 147–151]. Inspired by the bread baking process, a porous graphene film was fabricated through a leavening method reported by Niu et al. [147]. The filtered graphene oxide paper was used as “dough”, while the hydrazine vapor was the foaming and reducing agent (Fig. 7a). Hydrazine vapor could induce releasing gaseous species (such as H_2O and CO_2), resulting in formation of open pores (Fig. 7b, c). The specific capacitance of this rGO foam was 110 F g^{-1} . Upon bending it showed no significant difference in capacitive behaviour when the distance between two ends was changed from 3 to 2 cm (Fig. 7d, e).

Fig. 7 (a) Schematic procedures to fabricate rGO foam; (b, c) Cross-sectional SEM images of a rGO foam; (d) Schematic diagram of a flexible rGO foam supercapacitor; (e) Cyclic voltammograms of a rGO foam supercapacitor with or without bending [147].

Using graphene hydrogel to produce flexible electrodes with a 3D macroscopic structure is a simple and effective way [117, 148, 149]. Graphene sheets containing large amount of conjugated structures can offer many π - π stacking sites to form strong bonds. The partial overlapping of graphene sheets results in formation of graphene hydrogel [156]. Xu and co-workers reported an all-solid-state supercapacitor based on graphene hydrogel films, which were fabricated through a typical hydrothermal approach [117]. Squeezing out most of the entrapped water could increase contact within the graphene skeleton and still retained its 3D porous structure, which demonstrated an improved electric conductivity (Fig. 8a-d). The assembled flexible supercapacitor device with a thickness of $\sim 120\ \mu\text{m}$ and H_2SO_4 -PVA (polyvinyl alcohol) gel electrolyte displayed a high gravimetric capacitance of $186\ \text{F g}^{-1}$ and an enhanced areal capacitance of $372\ \text{mF cm}^{-2}$. A macroporous freeze-dried graphene hydrogel film was prepared by simply blade-casting GO hydrogel on a glass substrate in combination with a subsequent reduction in hydroiodic acid/acetic acid (HI/HAc) [148]. Such rGO film was mechanically strong and flexible, and the assembled flexible supercapacitor device displayed a very stable capacitive performance at various bending angles. Graphene hydrogel could be spontaneously formed on the surface of a relatively active metal such as zinc, and GO was simultaneously reduced in the dispersion (Fig. 8e-h) [149]. Graphene sheets were interconnected in a quasi-parallel manner to form an open porous structure, with pore size ranging from tens of nanometers to several micrometers. This method can be used to produce graphene hydrogel films with different shapes at large scale. The assembled supercapacitor displayed a high areal capacitance of $33.8\ \text{mF cm}^{-2}$ at $1\ \text{mA cm}^{-2}$, and a high capacity retention rate of 97.8% over 4,000 charge/discharge cycles.

Fig. 8 (a) Schematic illustration and (b) photos of the fabrication process of flexible solid state supercapacitors using graphene hydrogel films; SEM images of the porous structure of the film before (c) and after (d) pressing [113]. (e) Graphene gelation procedure on a Zn plate; (f) SEM image of the freeze-dried graphene gel; (g) Large-scale production of graphene gel; (h) Availability of graphene gel to form different shapes [149].

Chemical activation is another commonly applied method to generate porous graphene with a high SSA. Such an approach results in micro- or mesopores within the basal plane of the graphene sheets. Zhang et al. reported a free-standing and flexible porous graphene film fabricated through KOH activation [150]. Such film with a mixture of micropores (~ 1 nm) and mesopores (~ 3.6 nm) exhibited an ultra-high SSA of $2,400 \text{ m}^2 \text{ g}^{-1}$ and an in-plane electrical conductivity of $5,880 \text{ S m}^{-1}$. When applied in supercapacitor devices, it showed a high specific capacitance of 120 F g^{-1} at a high current density of 10 A g^{-1} in organic electrolyte

(tetraethylammonium tetrafluoroborate/acetonitrile, TEABF₄/AN). Duan's group reported a 3D hydrogel that was prepared by hydrothermal treatment of a GO dispersion in the presence of H₂O₂ [151]. The H₂O₂-activated graphene sheets showed in-plane holes, resulting in a high SSA of 1560 m² g⁻¹. The holey graphene film electrode delivered a gravimetric capacitance of 298 F g⁻¹ and a volumetric capacitance of 212 F cm⁻³ in organic electrolyte (EMIMBF₄/AN).

3.3. Integration of pseudocapacitive materials with the flexible graphene scaffold

To further increase the capacitance of flexible graphene electrodes, pseudo-capacitive materials including organic [157–161] or inorganic materials [38, 162–165] are introduced and anchored onto the graphene films or hydrogels. Cong et al. electrochemically synthesized PANi nanorod arrays on the surface of free-standing graphene paper (Fig. 9a-d), to deliver a high specific capacitance of 763 F g⁻¹ [157]. Paper-like graphene hydrogel can be used as substrate for growth of PPy via electropolymerization [160]. The surface energy of the graphene paper allowed the penetration of pyrrole monomer into the interior structure and subsequent polymerization, resulted in a layered structure. The resulting flexible composite paper showed an areal capacitance of 440 mF cm⁻² at 0.5 A g⁻¹. In the work by He et al. (Fig. 9e-h), a 3D macroporous graphene network was prepared by CVD growth of graphene on a nickel foam substrate [38]. After removal of Ni foam, the graphene network was used as substrate for electrodeposition of MnO₂, with a large mass loading of 9.8 mg cm⁻². The resulting foam-like graphene/MnO₂ composite displayed excellent flexibility as well as good electrochemical performance: a high areal capacitance of 1.42 F cm⁻² at a scan rate of 2 mV s⁻¹ in a three-electrode system; a capacitance of 130 F g⁻¹ in a flexible all-solid-state device.

Fig. 9 Schematic illustration of the fabrication process (a), photo (b), and SEM image (c) of a graphene/PANi paper; (d) CV curves of a graphene paper, PANi film and graphene/PANi paper at 10 mV s⁻¹ in 1 M H₂SO₄ [157]. (e) Photo of a flexible graphene/MnO₂ electrode; (f) SEM image shows the inner structure of MnO₂ coated graphene networks; (g) Schematic illustration and photos of a flexible supercapacitor using graphene/MnO₂ films; (h) CVs of the flexible supercapacitor at various scan rates. Inset shows the CVs at bending angles of 0° and 90° at 10 mV/s [38].

4. Transition metal dichalcogenides (TMDs) for flexible supercapacitors

Transition metal dichalcogenides (TMDs) is a group of two-dimensional (2D) compounds within the formula MX₂, in which MX₂ layers are held together by weak Van der Waals interactions [166–168]. Single MX₂ layers were formed by a layer of transition metal atoms from group 4, 5 or 6 (such as Mo or W) sandwiched by two layers of chalcogen atoms (such as S or Se) via

strong covalent bond [167–170]. Such a layer structure could be easily exfoliated to single layer MX_2 nanosheets, benefiting the capacitive behaviour by increasing contact area with electrolyte and storage of electrolyte ions [171, 172]. Moreover, inherent electrochemistry of TMDs offers large oxidative and reductive current signals upon potential scanning [168, 173]. Many efforts have been made to fabricate flexible supercapacitors using these 2D TMDs materials, especially molybdenum disulfide (MoS_2).

Being a representative member of the 2D TMD family, MoS_2 has attracted increasing attention in supercapacitors mainly due to its earth abundance, unique structure and high capacitance [166, 174, 175]. 2H- MoS_2 with a triangular prism crystalline structure (Fig. 10a) is a semi-conducting material [65] demonstrating poor rate capability. After chemically exfoliated by organolithium, metallic 1T- MoS_2 (octahedral structure) dominates in the single layer of MoS_2 nanosheets [65, 171, 176, 177]. The large surface area of MoS_2 nanosheets provides more active sites for charge storage in electrochemical double layer capacitors, while its large interlayer distance of 0.65 nm (Fig. 10b) facilitates ions insertion for high capacitance [171, 175]. Moreover, MoS_2 has the potential to offer pseudo-capacitances due to the wide range of oxidation state of Mo atom in MoS_2 [175].

Fig. 10 (a) Crystal structures of MoS₂ in 2H phase (left) and 1T phase (right) [178]; (b) Schematic illustration of multilayered MoS₂ with an interlayer spacing of ~0.65 nm [166]; (c) Photographs of thick 1T MoS₂ film on rigid glass and a flexible polyimide substrate, side view of the film observed by SEM, capacitance retention after 5,000 cycles in 0.5 M Li₂SO₄, H₂SO₄ and 1 M TEABF₄ in acetonitrile [65]; (d) Schematic diagram of the interdigital electrodes with MoS₂@SrGO active materials using the gravure printing technique and its electrochemical performance under repeated bending [179].

2D MoS₂ nanomaterials can be fabricated via three main methods: chemical vapor deposition (CVD) [180–182], hydrothermal synthesis [183, 184] and exfoliation [65, 185]. CVD can be used to grow high-quality MoS₂ materials followed by transferring onto flexible substrates for application in flexible supercapacitors [182]. However, the high cost and low productivity limit mass production. The latter two methods normally produce MoS₂ of small dimensions and relatively low aspect ratio limiting the formation of flexible free-standing MoS₂ papers [176]. A number of supporting materials have been used as substrates or skeletons to form MoS₂ based flexible electrodes, including non-conductive polymers [65] and papers [185], highly conductive carbon materials [186, 187] and metals [184].

Chhowalla et al. [65] reported a flexible MoS₂ film prepared by vacuum filtration of exfoliated MoS₂ nanosheets in combination with a subsequent transfer process onto a polyimide substrate. This film had a high content of metallic 1T phase MoS₂ and delivered a high capacitance ranging from ~400 to ~700 F cm⁻³ at a scan rate of 20 mV s⁻¹ in a variety of aqueous electrolytes. It also showed great cycling stability with a capacitance retention rate greater than 93% in neutral electrolytes and over 97% in acidic electrolytes over 5,000 cycles (Fig. 10c). It should be noted that the electrochemical performance was tested in a three-electrode system, and no assembled flexible supercapacitor was demonstrated. With a carbon cloth (CC) substrate hydrothermal synthesised MoS₂ hierarchical nanospheres electrodes delivered a high capacitance of 368 F g⁻¹ at a scan rate of 5 mV s⁻¹ in a solid-state flexible supercapacitor [186]. The hierarchical MoS₂ nanospheres on a carbon fiber produced via a hydrothermal method delivered a remarkable electrochemical performance: a high capacitance of 55.21 F cm⁻³ at a scan rate of 5 mV s⁻¹; superior cycling stability with a over 97% capacitance retention rate over 6,000 cycles at a high

current density of 2.21 A g^{-1} [187]. The annealed metal Ti wire was used as a substrate to fabricate flexible Ti/TiO₂/MoS₂ coaxial fiber electrode with hydrothermally grown MoS₂ nanosheets and a TiO₂ buffer layer underneath [184]. The assembled symmetric all-solid-state fiber supercapacitor demonstrated a high specific capacitance (70.6 F cm^{-3}).

Exfoliated 1T-MoS₂ nanosheets tend to retack resulting in poor capacitive performance, while the semiconducting 2H MoS₂ shows poor rate capability owing to its low conductivity [171, 175]. One common strategy to prevent the restacking is to incorporate nanomaterials as spacers between the nanosheets including graphene [176, 188, 189], carbon nanotubes [183, 185, 190] and conducting polymers [175]. The synergistic effect from the hybrid structure formed between introduced foreign matters and MoS₂ could augment the electrochemical performance. Graphene, a 2D layered carbon materials with large aspect ratio and remarkable mechanical properties, matches well with 2D MoS₂ nanosheets and are ideal for fabricating flexible MoS₂/graphene composites. For example, flexible MoS₂-graphene film [188] produced using vacuum filtration of a dispersion containing commercial graphene powder and exfoliated MoS₂ nanosheets achieved a capacitance of $\sim 11 \text{ mF cm}^{-2}$ at 5 mV s^{-1} with a significantly increased specific capacitance (up to 800%) during 10,000 cycling in a symmetrical coin cell arrangement in an aqueous electrolyte (Na₂SO₄). Using 3D nickel foam as a sacrificial template, the CVD grown graphene was used to produce 3D flexible graphene/MoS₂ composite [189] via hydrothermal method, followed by a transfer process onto an elastic polydimethylsiloxane (PDMS). The assembled stretchable all-solid-state supercapacitor delivered a capacitance of 19.44 F cm^{-3} (70.00 mF cm^{-2}) at a discharge current of 1.0 mA . Through gravure printing technique, a MoS₂@S-rGO microsupercapacitor [179] was fabricated affording a high specific capacitance

(6.56 mF cm⁻² at 35 μA cm⁻² in KOH-PVA electrolyte), a high energy density (0.58 mWh cm⁻³), and a high power density (13.4 mW cm⁻³). This printed microsupercapacitor lost only 9% of the maximum capacitance after 1,000 bending cycles (Fig. 10d).

Carbon nanotubes (CNTs) have been used to create MoS₂-based composites due to its high mechanical properties with excellent electrical conductivity and high surface area. The MoS₂/CNTs hybrid electrode formed by dip-coating on paper was highly flexible, and the assembled supercapacitors displayed a capacitance of 37 mF cm⁻² at a scan rate of 20 mV s⁻¹ (Fig. 11a) [185]. The dispersion of MoS₂ obtained via hydrothermal synthesis was coated onto a PDMS substrate pre-coated with a layer of CVD grown CNTs for application in stretchable supercapacitors (Fig. 11b). It delivered a high specific capacitance (13.16 F cm⁻³ at a current of 0.1 mA) as well as a high cycling retention rate (98%) over 10,000 charge-discharge processes. This film could even maintain its electrochemical performance when it was stretched from 0 to 240% at a speed of 3 mm per min, and retained 96% and 91% of the initial capacitance after being subjected to an elongation-relaxation process with an applied strain of 100% and 160% over 500 cycles [190]. Introduction of foreign pseudocapacitive inorganic matters can further improve the performance. A ternary system composite CoS₂/MoS₂/CC was developed by growing 3D hierarchical nanostructure CoS₂/MoS₂ nanocomposites on CC via hydrothermal synthesis [191]. The doping of conductive CoS₂ nanoparticles could efficiently lower the internal resistance and provide perfect continuous channels for electron transport, resulting in good electrochemical performance in supercapacitors.

Fig. 11 (a) Schematic diagram showing the formation process of MoS₂/CNT hybrid ink and electrode; digital image of a flexible paper-based electrode and electrochemical performance in a all-solid supercapacitors [185]. (b) Schematic fabrication process of a CNT/MoS₂ composite film for flexible and stretchable supercapacitor; its electrochemical performance in a flexible supercapacitor under different bending angles [190].

As mentioned above, free-standing films are highly desirable to achieve high gravimetric and volumetric capacitance owing to the elimination of dead weight and volume. However, it is difficult to fabricate free-standing MoS₂ films using the exfoliated MoS₂ nanosheets due to their relatively low aspect ratio and the lack of functional groups. Very recently free-standing MoS₂

films and fibers were fabricated from liquid crystalline MoS₂ dispersions, but no report for application in supercapacitors has appeared [174]. Free-standing MoS₂ based composites films can be obtained by incorporation with nanomaterials possessing the properties of mechanical flexibility and/or superior conductivity such as carbon materials and conducting polymers. Carbon materials, 2D graphene [176] and 1D carbon nanotubes [183, 192], are all used as structural materials in formation of free-standing MoS₂-based films. A flexible MoS₂/rGO hybrid films was fabricated via filtration of the suspension containing chemical exfoliated MoS₂ nanosheets and graphene oxide nanosheets in combination with a subsequent annealing process. It showed a high volumetric capacitance (380 F cm⁻³ at 10 mV s⁻¹), superior rate capability, and long cycle life (a 95% retention rate over 10,000 cycles) [176]. Chen's group [192] fabricated a flexible fiber shape symmetric supercapacitor using wet-spun rGO-MoS₂ hybrid fibers, which exhibited a capacitance of 30 F cm⁻³ at a current of 0.1 μA. Hao et al. [183] introduced both graphene and CNT to form a flexible tertiary MoS₂@CNT/RGO film (Fig. 12b). The assembled all-solid-state supercapacitor demonstrated an excellent cycling performance (a capacitance retention rate of 94.7% over 10,000 cycles at a current density of 10 mA cm⁻²), and a high capacitance (29.7 mF cm⁻² at 0.1 mA cm⁻²). Highly conductive poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was employed to fabricate a robust flexible MoS₂/PEDOT composites film via vacuum filtration by Yu et al. (Fig. 12c) [175]. PEDOT functioned as supporting medium and conducting platform for charge transport. It could deliver a high volumetric capacitance of 150.9 F cm⁻³ and 137.2 F cm⁻³ at a bending angle of 90° and 180°; a capacitance of 125.1 F cm⁻³ over 1000 bending times at 90° in a gel electrolyte PVA/H₃PO₄ at a scan rate of 50 mV s⁻¹.

Fig. 12 (a) Schematic illustration of the fabrication process of MoS₂@CNT/RGO electrode and its cycling performance measured at 10 mA cm⁻² [183]; (b) Cross-sectional view of a MoS₂/PEDOT film, cyclic voltammograms of a MoS₂/PEDOT film based supercapacitor at different bending angles and cycles at a scan rate of 50 mV s⁻¹ [175].

Besides MoS₂, other TMDs based flexible electrodes have also been developed such as WS₂ and VS₂. Vertical core/shell WS₂ nanowires was prepared by oxidation of Mo foil coupled with a subsequent sulfurization process [193]. The flexible supercapacitor using this type of 1D/2D core/shell nanowires electrodes delivered a capacitance of 18.3 mF/cm² at a scan rate of 5 mV/s. Xie's group [76] developed an ammonia-assisted strategy to exfoliate bulk VS₂ flakes into ultrathin VS₂ nanosheets stacked with less than five S-V-S single layers. These VS₂ nanosheets were used to construct in-plane supercapacitors, affording a specific capacitance of 4760 μF/cm² at 0.1 A/m² (150 nm thickness in-plane configuration with a geometric area of 11.52 cm²) and no obvious degradation even after 1000 charge/discharge cycles.

5. MXenes for flexible supercapacitors

Transition metal carbides, nitrides and carbonitrides are collectively referred as MXenes. Their general formula is $M_{n+1}X_nT_x$ ($n = 1-3$), where M represents an early transition metal, X is carbon and/or nitrogen, and T_x stands for the surface terminations (i.e. OH, O or F). They were fabricated by extraction of A from the layer structured MAX (A, an A group element) and exfoliation of the reaction products [194, 195]. The first reported MXene member was $Ti_3C_2T_x$ in 2011 [194]. Same as MAX, phases of Mxenes are layered hexagonal with $P6_3/mmc$ symmetry, where the M layers are nearly closed packed, and X atoms fill the octahedral sites as illustrated in Fig. 13(a) [194, 196].

Being a 2D material, Mxenes possesses the merits of large surface-to-volume ratio, rich chemistry, structural variety, good electrical conductivity with a hydrophilic surface. A variety of mono- and multivalent cation such as Li^+ , Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Al^{3+} can be intercalated electrochemically into MXenes [197–199], facilitating charge transport as an energy storage material. An asymmetric electrochemical cell composed of Ti_2CT_x anode and activated carbon cathode exhibited a maximum energy density of 30 Wh kg^{-1} at 930 W kg^{-1} in an organic electrolyte (1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate) over an operating window of 1.0 V and 3.5 V. It also displayed good capacity retention during 1000 galvanostatic charge/discharge cycles at rates up to 10C [200].

Free-standing MXenes films have been considered as promising electrodes for flexible supercapacitors owing to their large volumetric capacitances since carbides are much denser than carbons [196, 199, 201]. They can be easily fabricated via filtration of the dispersion of MXene

nanosheets (Fig. 13a, b), as that for graphene. The obtained flexible hydrophilic conductive and additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ paper displayed a specific surface area of $98 \text{ m}^2 \text{ g}^{-1}$, and delivered a volumetric capacitance of 340 F cm^{-3} [199], comparable to the best performance of carbon-based electrodes around 300 F cm^{-3} [202, 203]. It also demonstrated a superior cycling stability: no degradation in performance over 10,000 cycles at 1 A/g . This paper can also be produced using a delamination method in combination with a simple rolling process. $\text{Ti}_3\text{C}_2\text{T}_x$ produced by etching aluminium from Ti_3AlC_2 in a solution of lithium fluoride and hydrochloric acid swelled in volume like a clay when hydrated, and can be directly rolled into films ten of micrometers thick for use as electrode (Fig. 13c) [201]. This rolled film delivered extraordinary supercapacitive performances in a H_2SO_4 electrolyte: a capacitance up to 900 F cm^{-3} or 245 F g^{-1} ; no measurable capacitance loss even after 10,000 cycles; and a near 100% Coulombic efficiency.

Fig. 13 (a) Schematic illustration of MXenes with three different formulas, M_2X , M_3X_2 and M_4X_3 [196]; (b) Schematic fabrication of a free-standing Ti_3C_2 electrode including a

delamination and filtration process, and images of the electrode [199]; (c) Schematic synthesis of a $\text{Ti}_3\text{C}_2\text{T}_x$ clay from $\text{Ti}_3\text{AlC}_2\text{T}_x$, and the clay can be rolled to produce a flexible free-standing film [201].

The typical irreversible aggregation and face-to-face self-stacking phenomenon for 2D materials can also occur during the drying process of MXene nanosheets, which results in limitations in the electrochemical performance. The incorporation of a second or a third component can effectively prevent the self-restacking and improve the performance, and in particular using those conductive and/or pseudocapacitive materials, such as graphene [204–206], carbon nanotubes [207, 208], conducting polymers [209] and metal oxides [210, 211] has proven useful.

Graphene is the mostly used component in MXene composites owing to the high electrical conductivity and same 2D sheet feature for easy processability. Recently, Feng and co-workers fabricated MXene/graphene ($\text{T}_3\text{C}_2\text{T}_x/\text{EG}$) flexible films through vacuum-filtrating the suspension containing exfoliated MXene and electrochemically exfoliated graphene nanosheets [205]. These composite electrodes were assembled into flexible all solid-state supercapacitors, affording a volumetric capacitance of 216 F cm^{-3} at 0.1 A cm^{-3} . The microsupercapacitor fabricated by spray coating a composite ink delivered a large areal capacitance and volumetric capacitance as high as 3.26 mF cm^{-2} and 33 F cm^{-3} at 5 mV s^{-1} in a PVA/ H_3PO_4 gel electrolyte (Fig. 14a), superior to the state-of-the-art graphene-based microsupercapacitors. The $\text{T}_3\text{C}_2\text{T}_x$ /graphene film fabricated via the same filtration method but using the chemically exfoliated graphene instead also demonstrated a high volumetric and gravimetric capacitance of 370 F cm^{-3} and 405 F g^{-1} at 1 A g^{-1} in 6 M KOH [204].

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To form an ideal structure with alternating MXene/graphene layers, Gogosti and co-workers demonstrated the fabrication of flexible and highly conductive MXene/reduced graphene oxide ($\text{T}_3\text{C}_2\text{Tx/rGO}$) films through electrostatic self-assembly of negatively charged MXene nanosheets and positively charged rGO nanosheets with cationic polymer poly(diallyldimethylammonium chloride) (PDDA) (Fig. 14b) [206]. This composite efficiently alleviated restacking of both rGO and MXene, maintaining an ultrahigh electrical conductivity ($2,261 \text{ S cm}^{-1}$) and high density (3.1 g cm^{-3}). The rGO nanosheets acted as conductive spacers while increasing the interlayer spacing of MXene, providing unimpeded channels for electrolyte ions and ensuring high-rate performance. As a result, this flexible film delivered an impressive performance: a very high volumetric capacitance up to 1040 F cm^{-3} at 2 mV s^{-1} in $3 \text{ M H}_2\text{SO}_4$ with 61% of the capacitance attainable at 1 V s^{-1} ; excellent cyclability with almost no capacitance degradation over 20,000 cycles; an outstanding volumetric energy density of 32.6 Wh L^{-1} and an ultrahigh volumetric power density of 74.4 kW L^{-1} .

Fig. 14 (a) Schematic fabrication process of MXene/graphene ($\text{Ti}_3\text{C}_2\text{Tx}/\text{EG}$) film, and demonstration of the assembled micro-supercapacitors and its electrochemical performance [205]. (b) Schematic fabrication process of MXene/reduced graphene oxide ($\text{Ti}_3\text{C}_2\text{Tx}/\text{rGO}$) film electrode and its electrochemical performance [206].

Polypyrrole (PPy), a conducting polymer, was used to form a free-standing conductive hybrid film with MXene ($\text{Ti}_3\text{C}_2\text{Tx}$) via electropolymerization [209]. The presence of MXene Ti_3C_2 effectively prevented dense PPy stacking facilitating electrolyte infiltration; strong bonds, formed between the PPy backbone and the surface of Ti_3C_2 , not only ensured good conductivity but also provided precise pathways for charge-carrier transport. This film electrode delivered a high volumetric capacitance of 406 F cm^{-3} with a near 100% capacitance retention rate even after 20,000 charging/discharging cycles. The ultra-thin all-solid-state supercapacitor fabricated using this film electrode showed a high capacitance of 35 mF cm^{-2} and stable performance even when bent.

As aforementioned, CNTs can prevent the restacking of 2D graphene or MoS_2 nanosheets leading to greatly improved performance in supercapacitors [212–214]. The incorporation of CNTs into MXene nanosheets was also demonstrated, which could improve accessible surface area to ions for high capacitance and rate performance. The MXene/CNT paper fabricated via alternative deposition of MXene and CNT layers demonstrated a high volumetric capacitance of $\sim 390 \text{ F cm}^{-3}$ at a high current density of 5 A g^{-1} ; excellent cycling performance with no degradation over 10,000 cycles [208]. The capacitance of Ti_3C_2 film was increased 3-fold up to 245 F cm^{-3} with the incorporation of CNTs [211]. The decoration of MXene nanosheets with

pseudocapacitive metal oxides nanoparticles has also demonstrated an enhanced performance [210,211]. Kong and co-workers produced a $\text{MnO}_x\text{-Ti}_3\text{C}_2$ film via filtration of their dispersion, in which MnO_x was *in situ* formed and anchored on the surface of Ti_3C_2 nanolayers through electrostatic interaction. This film electrode delivered a high volumetric capacitance of 602 F cm^{-3} at 2 mV s^{-1} in $1 \text{ M Li}_2\text{SO}_4$ [211].

6. Summary and perspectives

In this review article, recent progress in flexible supercapacitors based on 2D materials has been reviewed. The high aspect ratio and mechanical flexibility of these atomically thin sheets provides a unique environment for the assembly of thin film structures required for fabrication of flexible supercapacitors. Self-stacking of these 2D nanosheets owing to the strong van der Waals interaction between adjacent nanosheets can be effectively alleviated by creating new compositions with other nanomaterials or by forming novel 3D porous structures.

Significant progress has been made in fabrication of flexible and light-weight supercapacitors using these 2D materials over recent years. However, some challenges still remain if we are to produce flexible robust supercapacitors with high energy density, high power density, excellent cycling stability and low cost. For example, control of the quality of 2D nanosheets produced via wet-chemistry approaches remains a challenge. Strong and stable interaction between electrolyte and electrode in particular during long term deformation process is critical to high performance flexible supercapacitors. With creation of 3D porous structures to enable high energy and power density, the volumetric capacitance and mechanical flexibility are often compromised.

Apart from novel electrode materials, safe electrolytes with a wide electrochemical window such as ionic liquid are highly desirable for achieving high energy density. In addition, to achieve energy autonomy (i.e. self-powered integrated circuits or microelectromechanical systems) the integration of supercapacitors with solar, thermal or mechanical energy harvesting systems is to be pursued. Supercapacitor is an energy storage component to compensate for the intermittency generated by those renewable sources, and provide consistent power to deployed devices [215,216]. The downscaling of electronic devices and power sources to micro scale is the direction, which may be achieved by three dimensional (3D) printing, a layer-by-layer technology. It has emerged as an innovative approach to fabricating energy storage devices from macroscale down to nanoscale [217,218]. It provides freedom and accurate control over the device geometry and architecture, which will greatly promote the development of micro-scaled supercapacitors and the integration with energy generators.

We must continue to consider the whole pipeline from source processing of 2D materials, fabrication approaches to final products if practical devices are to be realized.

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References

- [1] J. Gubbi, R. Buyya, S. Marusic, M. Palaniswami, Future generation computer systems, 29 (2013) 1645-1660.
- [2] F. Carpi, D. De Rossi, IEEE transactions on Information Technology in biomedicine, 9 (2005) 295-318.
- [3] J.A. Rogers, T. Someya, Y. Huang, Science, 327 (2010) 1603-1607.
- [4] D.J. Lipomi, Z. Bao, Energy & Environmental Science, 4 (2011) 3314-3328.
- [5] H. Nishide, K. Oyaizu, Science, 319 (2008) 737-738.
- [6] D. Larcher, J.M. Tarascon, Nature chemistry, 7 (2015) 19-29.
- [7] M. Armand, J.M. Tarascon, Nature, 451 (2008) 652-657.
- [8] P. Poizot, F. Dolhem, Energy & Environmental Science, 4 (2011) 2003-2019.
- [9] H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J.M. Tarascon, ChemSusChem, 1 (2008) 348-355.
- [10] J.M. Tarascon, M. Armand, Nature, 414 (2001) 359-367.
- [11] J.B. Goodenough, Y. Kim, Chemistry of materials, 22 (2009) 587-603.
- [12] B. Scrosati, J. Garche, Journal of Power Sources, 195 (2010) 2419-2430.
- [13] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, Energy & Environmental Science, 4 (2011) 3243-3262.
- [14] G. Zhou, F. Li, H.M. Cheng, Energy & Environmental Science, 7 (2014) 1307-1338.
- [15] H. Gwon, J. Hong, H. Kim, D.H. Seo, S. Jeon, K. Kang, Energy & Environmental Science, 7 (2014) 538-551.
- [16] P.G. Bruce, B. Scrosati, J.M. Tarascon, Angewandte Chemie International Edition, 47 (2008) 2930-2946.

- [17] S.M. Whittingham, Chemical reviews, 104 (2004) 4271-4302.
- [18] M. Reddy, G. Subba Rao, B. Chowdari, Chemical reviews, 113 (2013) 5364-5457.
- [19] Z. Song, H. Zhou, Energy & Environmental Science, 6 (2013) 2280-2301.
- [20] Y. Liang, Z. Tao, J. Chen, Advanced Energy Materials, 2 (2012) 742-769.
- [21] P. Novák, K. Müller, K. Santhanam, O. Haas, Chemical Reviews, 97 (1997) 207-282.
- [22] R. Holze, Y. Wu, Electrochimica acta, 122 (2014) 93-107.
- [23] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, G. Shen, Advanced materials, 26 (2014) 4763-4782.
- [24] K. Xie, B. Wei, Advanced materials, 26 (2014) 3592-3617.
- [25] C. Wang, G.G. Wallace, Electrochimica Acta, 175 (2015) 87-95.
- [26] K. Jost, G. Dion, Y. Gogotsi, Journal of Materials Chemistry A, 2 (2014) 10776-10787.
- [27] L. Nyholm, G. Nyström, A. Mihranyan, M. Strømme, Advanced materials, 23 (2011) 3751-3769.
- [28] Y.Z. Zhang, Y. Wang, T. Cheng, W.Y. Lai, H. Pang, W. Huang, Chemical Society reviews, 44 (2015) 5181-5199.
- [29] S.Y. Lee, K.H. Choi, W.S. Choi, Y.H. Kwon, H.R. Jung, H.C. Shin, J.Y. Kim, Energy & Environmental Science, 6 (2013) 2414-2423.
- [30] B.E. Conway, Journal of the Electrochemical Society, 138 (1991) 1539-1548.
- [31] Y. Wang, Y. Xia, Advanced materials, 25 (2013) 5336-5342.
- [32] Y. Wang, Y. Song, Y. Xia, Chemical Society reviews, 45 (2016) 5925-5950.
- [33] Z. Yu, L. Tetard, L. Zhai, J. Thomas, Energy Environ. Sci., 8 (2015) 702-730.
- [34] H. Choi, H. Yoon, Nanomaterials, 5 (2015) 906-936.
- [35] M. Vangari, T. Pryor, L. Jiang, Journal of Energy Engineering, 139 (2013) 72-79.

- [36] M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, *Nanoscale*, 5 (2013) 72-88.
- [37] A.S. Aricò, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, *Nature materials*, 4 (2005) 366-377.
- [38] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E. Xie, *ACS nano*, 7 (2013) 174-182.
- [39] F. Liu, S. Song, D. Xue, H. Zhang, *Advanced Materials*, 24 (2012) 1089-1094.
- [40] Q. Lu, J.G. Chen, J.Q. Xiao, *Angew Chem Int Ed Engl*, 52 (2013) 1882-1889.
- [41] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, *Advanced materials*, 24 (2012) 5979-6004.
- [42] Z. Fan, Q. Zhao, T. Li, J. Yan, Y. Ren, J. Feng, T. Wei, *Carbon*, 50 (2012) 1699-1703.
- [43] Y. Wang, Y. Lei, J. Li, L. Gu, H. Yuan, D. Xiao, *ACS Appl. Mater. Interfaces*, 6 (2014) 6739-6747.
- [44] M. Fan, B. Ren, L. Yu, Q. Liu, J. Wang, D. Song, J. Liu, X. Jing, L. Liu, *CrystEngComm*, 16 (2014) 10389-10394.
- [45] X.Y. Yu, L. Yu, X.W.D. Lou, *Advanced Energy Materials*, 6 (2016) 1501333.
- [46] Y. Liu, X. Peng, *Applied Materials Today*, 8 (2017) 104-115.
- [47] X. Peng, L. Peng, C. Wu, Y. Xie, *Chemical Society reviews*, 43 (2014) 3303-3323.
- [48] J.E. Kim, J.H. Oh, M. Kotal, N. Koratkar, I.K. Oh, *Nano Today*, (2017) 100-123.
- [49] H. Wang, H. Yuan, S. Sae Hong, Y. Li, Y. Cui, *Chemical Society reviews*, 44 (2015) 2664-2680.
- [50] A.H. Khan, S. Ghosh, B. Pradhan, A. Dalui, L.K. Shrestha, S. Acharya, K. Ariga, *Bulletin of the Chemical Society of Japan*, 90 (2017) 627-648.
- [51] H. Zhang, *ACS nano*, 9 (2015) 9451-9469.
- [52] W. Yang, X. Zhang, Y. Xie, *Nano Today*, (2016) 793-816.

- [53] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *science*, 306 (2004) 666-669.
- [54] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, J. Hone, *Nat Nanotechnol*, 5 (2010) 722-726.
- [55] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D.W. Fam, A.I. Tok, Q. Zhang, H. Zhang, *Small*, 8 (2012) 63-67.
- [56] H. Li, J. Wu, Z. Yin, H. Zhang, *Acc Chem Res*, 47 (2014) 1067-1075.
- [57] D.J. Late, B. Liu, H.S.S.R. Matte, C.N.R. Rao, V.P. Dravid, *Advanced Functional Materials*, 22 (2012) 1894-1905.
- [58] K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O.M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S.E. O'Brien, E.K. McGuire, B.M. Sanchez, G.S. Duesberg, N. McEvoy, T.J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J.N. Coleman, *Nat Mater*, 13 (2014) 624-630.
- [59] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y.K. Gun'Ko, J.J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari, J.N. Coleman, *Nat Nanotechnol*, 3 (2008) 563-568.
- [60] U. Khan, P. May, A. O'Neill, A.P. Bell, E. Boussac, A. Martin, J. Semple, J.N. Coleman, *Nanoscale*, 5 (2013) 581-587.
- [61] D. Hanlon, C. Backes, T.M. Higgins, M. Hughes, A. O'Neill, P. King, N. McEvoy, G.S. Duesberg, B. Mendoza Sanchez, H. Pettersson, V. Nicolosi, J.N. Coleman, *Chemistry of Materials*, 26 (2014) 1751-1763.

- [62] J.R. Brent, N. Savjani, E.A. Lewis, S.J. Haigh, D.J. Lewis, P. O'Brien, *Chem Commun (Camb)*, 50 (2014) 13338-13341.
- [63] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, *Nature*, 490 (2012) 192-200.
- [64] L.M. Viculis, J.J. Mack, O.M. Mayer, H.T. Hahn, R.B. Kaner, *Journal of Materials Chemistry*, 15 (2005) 974-978.
- [65] M. Acerce, D. Voiry, M. Chhowalla, *Nature nanotechnology*, 10 (2015) 313-318.
- [66] Y. Zhu, L. Peng, D. Chen, G. Yu, *Nano letters*, 16 (2016) 742-747.
- [67] M.A. Lukowski, A.S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, *Journal of the American Chemical Society*, 135 (2013) 10274-10277.
- [68] M. Yi, Z. Shen, *J. Mater. Chem. A*, 3 (2015) 11700-11715.
- [69] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, *Science*, 331 (2011) 568-571.
- [70] R.J. Smith, P.J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G.S. Duesberg, J.C. Grunlan, G. Moriarty, J. Chen, J. Wang, A.I. Minett, V. Nicolosi, J.N. Coleman, *Adv Mater*, 23 (2011) 3944-3948.
- [71] Z. Zeng, T. Sun, J. Zhu, X. Huang, Z. Yin, G. Lu, Z. Fan, Q. Yan, H.H. Hng, H. Zhang, *Angew Chem Int Ed Engl*, 51 (2012) 9052-9056.
- [72] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang, *Angewandte Chemie International Edition*, 50 (2011) 11093-11097.
- [73] K. Parvez, Z.S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Mullen, *J Am Chem Soc*, 136 (2014) 6083-6091.

- [74] C. Wu, X. Lu, L. Peng, K. Xu, X. Peng, J. Huang, G. Yu, Y. Xie, *Nature communications*, 4 (2013) 2431.
- [75] C. Lin, X. Zhu, J. Feng, C. Wu, S. Hu, J. Peng, Y. Guo, L. Peng, J. Zhao, J. Huang, J. Yang, Y. Xie, *Journal of the American Chemical Society*, 135 (2013) 5144-5151.
- [76] J. Feng, X. Sun, C. Wu, L. Peng, C. Lin, S. Hu, J. Yang, Y. Xie, *J Am Chem Soc*, 133 (2011) 17832-17838.
- [77] W.S. Hummers Jr, R.E. Offeman, *Journal of the American Chemical Society*, 80 (1958) 1339-1339.
- [78] M.J. Allen, V.C. Tung, R.B. Kaner, *Chemical Reviews*, 110 (2010) 132-145.
- [79] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, *Nat Nano*, 3 (2008) 101-105.
- [80] C.D. Zangmeister, *Chemistry of Materials*, 22 (2010) 5625-5629.
- [81] H.-L. Guo, X.-F. Wang, Q.-Y. Qian, F.-B. Wang, X.-H. Xia, *ACS nano*, 3 (2009) 2653-2659.
- [82] Y. Shi, H. Li, L.J. Li, *Chemical Society reviews*, 44 (2015) 2744-2756.
- [83] A. Ambrosi, C.K. Chua, N.M. Latiff, A.H. Loo, C.H.A. Wong, A.Y.S. Eng, A. Bonanni, M. Pumera, *Chemical Society reviews*, 45 (2016) 2458-2493.
- [84] Q. Ji, Y. Zhang, Y. Zhang, Z. Liu, *Chemical Society reviews*, 44 (2015) 2587-2602.
- [85] C. Tan, H. Zhang, *Nature communications*, 6 (2015) 7873.
- [86] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, *Science*, 324 (2009) 1312-1314.
- [87] X. Li, C.W. Magnuson, A. Venugopal, R.M. Tromp, J.B. Hannon, E.M. Vogel, L. Colombo, R.S. Ruoff, *Journal of the American Chemical Society*, 133 (2011) 2816-2819.

- [88] L. Song, L. Ci, H. Lu, P.B. Sorokin, C. Jin, J. Ni, A.G. Kvashnin, D.G. Kvashnin, J. Lou, B.I. Yakobson, P.M. Ajayan, *Nano letters*, 10 (2010) 3209-3215.
- [89] S. Wang, X. Wang, J.H. Warner, *ACS Nano*, 9 (2015) 5246-5254.
- [90] G. Ning, W. Jinqian, F. Lili, J. Yi, L. Dayao, Z. Hongwei, W. Kunlin, W. Dehai, *Nanotechnology*, 23 (2012) 415605.
- [91] Y.H. Lee, X.Q. Zhang, W. Zhang, M.T. Chang, C.T. Lin, K.D. Chang, Y.C. Yu, J.T. Wang, C.S. Chang, L.J. Li, T.W. Lin, *Adv Mater*, 24 (2012) 2320-2325.
- [92] X. Lu, M.I. Utama, J. Lin, X. Gong, J. Zhang, Y. Zhao, S.T. Pantelides, J. Wang, Z. Dong, Z. Liu, W. Zhou, Q. Xiong, *Nano letters*, 14 (2014) 2419-2425.
- [93] Y.H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.K. Chang, W.T. Hsu, J.K. Huang, C.L. Hsu, M.H. Chiu, *ACS nano*, 8 (2014) 8582-8590.
- [94] H.R. Gutierrez, N. Perea-Lopez, A.L. Elias, A. Berkdemir, B. Wang, R. Lv, F. Lopez-Urias, V.H. Crespi, H. Terrones, M. Terrones, *Nano letters*, 13 (2013) 3447-3454.
- [95] J.K. Huang, J. Pu, C.L. Hsu, M.H. Chiu, Z.Y. Juang, Y.H. Chang, W.H. Chang, Y. Iwasa, T. Takenobu, L.J. Li, *ACS nano*, 8 (2013) 923-930.
- [96] Y. Zhang, Y. Zhang, Q. Ji, J. Ju, H. Yuan, J. Shi, T. Gao, D. Ma, M. Liu, Y. Chen, *ACS nano*, 7 (2013) 8963-8971.
- [97] M. Choucair, P. Thordarson, J.A. Stride, *Nat Nanotechnol*, 4 (2009) 30-33.
- [98] Y. Du, Z. Yin, J. Zhu, X. Huang, X.J. Wu, Z. Zeng, Q. Yan, H. Zhang, *Nature communications*, 3 (2012) 1177.
- [99] Z. Sun, T. Liao, Y. Dou, S.M. Hwang, M.S. Park, L. Jiang, J.H. Kim, S.X. Dou, *Nature communications*, 5 (2014) 3813.

- [100] X.J. Wu, X. Huang, X. Qi, H. Li, B. Li, H. Zhang, *Angew Chem Int Ed Engl*, 53 (2014) 8929-8933.
- [101] B. Mahler, V. Hoepfner, K. Liao, G.A. Ozin, *Journal of the American Chemical Society*, 136 (2014) 14121-14127.
- [102] J.S. Son, J.H. Yu, S.G. Kwon, J. Lee, J. Joo, T. Hyeon, *Advanced Materials*, 23 (2011) 3214-3219.
- [103] S. Eigler, M. Enzelberger-Heim, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Rockert, J. Xiao, C. Papp, O. Lytken, H.P. Steinruck, P. Muller, A. Hirsch, *Adv Mater*, 25 (2013) 3583-3587.
- [104] Y. Fang, Y. Lv, R. Che, H. Wu, X. Zhang, D. Gu, G. Zheng, D. Zhao, *Journal of the American Chemical Society*, 135 (2013) 1524-1530.
- [105] K. Zhang, H.J. Kim, X. Shi, J.T. Lee, J.M. Choi, M.S. Song, J.H. Park, *Inorganic chemistry*, 52 (2013) 9807-9812.
- [106] H. Liang, F. Meng, M. Caban-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang, S. Jin, *Nano letters*, 15 (2015) 1421-1427.
- [107] L. Zhang, H. Yao, Z. Li, P. Sun, F. Liu, C. Dong, J. Wang, Z. Li, M. Wu, C. Zhang, B. Zhao, *Journal of Alloys and Compounds*, 711 (2017) 31-41.
- [108] Z. Fan, X. Huang, Y. Han, M. Bosman, Q. Wang, Y. Zhu, Q. Liu, B. Li, Z. Zeng, J. Wu, W. Shi, S. Li, C.L. Gan, H. Zhang, *Nature communications*, 6 (2015) 6571.
- [109] X. Huang, S. Tang, X. Mu, Y. Dai, G. Chen, Z. Zhou, F. Ruan, Z. Yang, N. Zheng, *Nat Nanotechnol*, 6 (2011) 28-32.
- [110] S. Gao, Y. Sun, F. Lei, L. Liang, J. Liu, W. Bi, B. Pan, Y. Xie, *Angew Chem Int Ed Engl*, 53 (2014) 12789-12793.

- [111] Y. Sun, Z. Sun, S. Gao, H. Cheng, Q. Liu, J. Piao, T. Yao, C. Wu, S. Hu, S. Wei, Y. Xie, *Nature communications*, 3 (2012) 1057.
- [112] D. Yoo, M. Kim, S. Jeong, J. Han, J. Cheon, *Journal of the American Chemical Society*, 136 (2014) 14670-14673.
- [113] A.K. Geim, K.S. Novoselov, *Nat Mater*, 6 (2007) 183-191.
- [114] Y. Shao, M.F. El-Kady, L.J. Wang, Q. Zhang, Y. Li, H. Wang, M.F. Mousavi, R.B. Kaner, *Chemical Society Reviews*, 44 (2015) 3639-3665.
- [115] X. Yang, J. Zhu, L. Qiu, D. Li, *Advanced materials*, 23 (2011) 2833-2838.
- [116] X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, *Science*, 341 (2013) 534-537.
- [117] Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, X. Duan, *ACS nano*, 7 (2013) 4042-4049.
- [118] A. Yu, I. Roes, A. Davies, Z. Chen, *Applied Physics Letters*, 96 (2010) 253105.
- [119] Z. Weng, Y. Su, D.-W. Wang, F. Li, J. Du, H.-M. Cheng, *Adv Energy Mater*, 1 (2011) 917-922.
- [120] S. Zheng, X. Tang, Z.-S. Wu, Y.-Z. Tan, S. Wang, C. Sun, H.-M. Cheng, X. Bao, *Acs Nano*, 11 (2017) 2171-2179.
- [121] C. Zhao, K. Shu, C. Wang, S. Gambhir, G.G. Wallace, *Electrochim Acta*, 172 (2015) 12-19.
- [122] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, *Advanced materials*, 25 (2013) 2326-2331.
- [123] Y. Li, K. Sheng, W. Yuan, G. Shi, *Chemical communications*, 49 (2013) 291-293.
- [124] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, 5 (2014) 3754.
- [125] X. Wang, G. Shi, *Energy & Environmental Science*, 8 (2015) 790-823.

- [126] W.K. Chee, H.N. Lim, Z. Zainal, N.M. Huang, I. Harrison, Y. Andou, *The Journal of Physical Chemistry C*, 120 (2016) 4153-4172.
- [127] R.K.L. Tan, S.P. Reeves, N. Hashemi, D.G. Thomas, E. Kavak, R. Montazami, N.N. Hashemi, *J Mater Chem A*, 5 (2017) 17777-17803.
- [128] C. Wang, D. Li, C.O. Too, G.G. Wallace, *Chem Mater*, 21 (2009) 2604-2606.
- [129] D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H.B. Dommett, G. Evmenenko, S.T. Nguyen, R.S. Ruoff, *Nature*, 448 (2007) 457-460.
- [130] G. Wang, X. Sun, F. Lu, H. Sun, M. Yu, W. Jiang, C. Liu, J. Lian, *Small*, 8 (2012) 452-459.
- [131] L. Qiu, X. Yang, X. Gou, W. Yang, Z.-F. Ma, G.G. Wallace, D. Li, *Chemistry – A European Journal*, 16 (2010) 10653-10658.
- [132] L. Huang, C. Li, G. Shi, *Journal of Materials Chemistry A*, 2 (2014) 968-974.
- [133] K. Shu, C. Wang, M. Wang, C. Zhao, G.G. Wallace, *J Mater Chem A*, 2 (2014) 1325-1331.
- [134] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, *ACS nano*, 4 (2010) 1963-1970.
- [135] Y. Liu, B. Weng, J.M. Razal, Q. Xu, C. Zhao, Y. Hou, S. Seyedin, R. Jalili, G.G. Wallace, *J. Chen*, 5 (2015) 17045.
- [136] Y. Ge, C. Wang, K. Shu, C. Zhao, X. Jia, S. Gambhir, G.G. Wallace, *Rsc Adv*, 5 (2015) 102643-102651.
- [137] S. Li, K. Shu, C. Zhao, C. Wang, Z. Guo, G. Wallace, H.K. Liu, *Acs Appl Mater Inter*, 6 (2014) 16679-16686.
- [138] A. Sumboja, C.Y. Foo, X. Wang, P.S. Lee, *Advanced materials*, 25 (2013) 2809-2815.
- [139] M. Li, Z. Tang, M. Leng, J. Xue, *Advanced Functional Materials*, 24 (2014) 7495-7502.

- [140] C.-M. Chen, Q. Zhang, C.-H. Huang, X.-C. Zhao, B.-S. Zhang, Q.-Q. Kong, M.-Z. Wang, Y.-G. Yang, R. Cai, D. Sheng Su, *Chem Commun*, 48 (2012) 7149-7151.
- [141] B.G. Choi, M. Yang, W.H. Hong, J.W. Choi, Y.S. Huh, *ACS nano*, 6 (2012) 4020-4028.
- [142] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, H. Zhang, *Small*, 7 (2011) 3163-3168.
- [143] P. Yu, X. Zhao, Z. Huang, Y. Li, Q. Zhang, *Journal of Materials Chemistry A*, 2 (2014) 14413-14420.
- [144] J. Yan, Y. Ding, C. Hu, H. Cheng, N. Chen, Z. Feng, Z. Zhang, L. Qu, *Journal of Materials Chemistry A*, 2 (2014) 16786-16792.
- [145] S.H. Lee, H.W. Kim, J.O. Hwang, W.J. Lee, J. Kwon, C.W. Bielawski, R.S. Ruoff, S.O. Kim, *Angewandte Chemie International Edition*, 49 (2010) 10084-10088.
- [146] Y. Li, J. Chen, L. Huang, C. Li, J.-D. Hong, G. Shi, *Adv Mater*, 26 (2014) 4789-4793.
- [147] Z. Niu, J. Chen, H.H. Hng, J. Ma, X. Chen, *Advanced materials*, 24 (2012) 4144-4150.
- [148] Z. Xiong, C. Liao, W. Han, X. Wang, *Advanced materials*, 27 (2015) 4469-4475.
- [149] U.N. Maiti, J. Lim, K.E. Lee, W.J. Lee, S.O. Kim, *Advanced materials*, 26 (2014) 615-619.
- [150] L.L. Zhang, X. Zhao, M.D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, R.S. Ruoff, *Nano letters*, 12 (2012) 1806-1812.
- [151] Y. Xu, Z. Lin, X. Zhong, X. Huang, N.O. Weiss, Y. Huang, X. Duan, 5 (2014) 4554.
- [152] A.J. Heeger, *Angewandte Chemie International Edition*, 40 (2001) 2591-2611.
- [153] G.A. Snook, P. Kao, A.S. Best, *J Power Sources*, 196 (2011) 1-12.
- [154] Y. Huang, H. Li, Z. Wang, M. Zhu, Z. Pei, Q. Xue, Y. Huang, C. Zhi, *Nano Energy*, 22 (2016) 422-438.
- [155] R. Gangopadhyay, A. De, *Chemistry of materials*, 12 (2000) 608-622.

- [156] Y. Shi, J. Zhang, L. Pan, Y. Shi, G. Yu, *Nano Today*, 11 (2016) 738-762.
- [157] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, *Energ Environ Sci*, 6 (2013) 1185-1191.
- [158] K. Chi, Z. Zhang, J. Xi, Y. Huang, F. Xiao, S. Wang, Y. Liu, *ACS applied materials & interfaces*, 6 (2014) 16312-16319.
- [159] Y. Zhao, J. Liu, Y. Hu, H. Cheng, C. Hu, C. Jiang, L. Jiang, A. Cao, L. Qu, *Advanced materials*, 25 (2013) 591-595.
- [160] K. Shu, C. Wang, C. Zhao, Y. Ge, G.G. Wallace, *Electrochim Acta*, 212 (2016) 561-571.
- [161] X. Wu, M. Lian, *Journal of Power Sources*, 362 (2017) 184-191.
- [162] S. Cho, M. Kim, J. Jang, *ACS applied materials & interfaces*, 7 (2015) 10213-10227.
- [163] Z. Li, Y. Mi, X. Liu, S. Liu, S. Yang, J. Wang, *Journal of Materials Chemistry*, 21 (2011) 14706-14711.
- [164] M. Liu, J. Sun, *Journal of Materials Chemistry A*, 2 (2014) 12068-12074.
- [165] J. Kim, W.-H. Khoh, B.-H. Wee, J.-D. Hong, *Rsc Adv*, 5 (2015) 9904-9911.
- [166] N.A. Kumar, M.A. Dar, R. Gul, J.B. Baek, *Materials Today*, 18 (2015) 286-298.
- [167] A.H. Loo, A. Bonanni, Z. Sofer, M. Pumera, *Electrochemistry Communications*, 50 (2015) 39-42.
- [168] C.C. Mayorga-Martinez, A. Ambrosi, A.Y.S. Eng, Z. Sofer, M. Pumera, *Electrochemistry Communications*, 56 (2015) 24-28.
- [169] M. Yousaf, A. Mahmood, Y. Wang, Y. Chen, Z. Ma, R.P. Han, *Journal of Electrical Engineering*, 4 (2016) 58-74.
- [170] S.K. Balasingam, J.S. Lee, Y. Jun, *Dalton Transactions*, 44 (2015) 15491-15498.
- [171] Y. Chao, R. Jalili, Y. Ge, C. Wang, T. Zheng, K. Shu, G.G. Wallace, *Advanced Functional Materials*, 27 (2017) 1700234.

- [172] X. Zhang, L. Hou, A. Ciesielski, P. Samorì, *Advanced Energy Materials*, 6 (2016) 1600671-n/a.
- [173] A.Y.S. Eng, A. Ambrosi, Z. Sofer, P. Simek, M. Pumera, *ACS nano*, 8 (2014) 12185-12198.
- [174] R. Jalili, S. Aminorroaya-Yamini, T.M. Benedetti, S.H. Aboutalebi, Y. Chao, G.G. Wallace, D.L. Officer, *Nanoscale*, 8 (2016) 16862-16867.
- [175] Y. Ge, R. Jalili, C. Wang, T. Zheng, Y. Chao, G.G. Wallace, *Electrochimica Acta*, 235 (2017) 348-355.
- [176] S. Byun, D.M. Sim, J. Yu, J.J. Yoo, *ChemElectroChem*, 2 (2015) 1938-1946.
- [177] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano letters*, 11 (2011) 5111-5116.
- [178] R. Kappera, D. Voiry, S.E. Yalcin, B. Branch, G. Gupta, A.D. Mohite, M. Chhowalla, *Nature materials*, 13 (2014) 1128-1134.
- [179] Y. Xiao, L. Huang, Q. Zhang, S. Xu, Q. Chen, W. Shi, *Applied Physics Letters*, 107 (2015) 013906.
- [180] J. Jeon, S.K. Jang, S.M. Jeon, G. Yoo, Y.H. Jang, J.H. Park, S. Lee, *Nanoscale*, 7 (2015) 1688-1695.
- [181] V.K. Kumar, S. Dhar, T.H. Choudhury, S. Shivashankar, S. Raghavan, *Nanoscale*, 7 (2015) 7802-7810.
- [182] J. Pu, Y. Yomogida, K.K. Liu, L.J. Li, Y. Iwasa, T. Takenobu, *Nano letters*, 12 (2012) 4013-4017.
- [183] S. Wang, J. Zhu, Y. Shao, W. Li, Y. Wu, L. Zhang, X. Hao, *Chemistry*, 23 (2017) 3438-3446.

- [184] X. Li, X. Li, J. Cheng, D. Yuan, W. Ni, Q. Guan, L. Gao, B. Wang, *Nano Energy*, 21 (2016) 228-237.
- [185] A. Liu, H. Lv, H. Liu, Q. Li, H. Zhao, *Journal of Materials Science: Materials in Electronics*, 28 (2017) 8452-8459.
- [186] M.S. Javed, S. Dai, M. Wang, D. Guo, L. Chen, X. Wang, C. Hu, Y. Xi, *Journal of Power Sources*, 285 (2015) 63-69.
- [187] L. Gao, X. Li, X. Li, J. Cheng, B. Wang, Z. Wang, C. Li, *RSC Adv.*, 6 (2016) 57190-57198.
- [188] M.A. Bissett, I.A. Kinloch, R.A. Dryfe, *ACS applied materials & interfaces*, 7 (2015) 17388-17398.
- [189] N. Li, T. Lv, Y. Yao, H. Li, K. Liu, T. Chen, *J. Mater. Chem. A*, 5 (2017) 3267-3273.
- [190] L. Tian, Y. Yao, L. Ning, C. Tao, *Angew. Chem. Int. Ed.*, 55 (2016) 9191 –9195.
- [191] C. Su, J. Xiang, F. Wen, L. Song, C. Mu, D. Xu, C. Hao, Z. Liu, *Electrochimica Acta*, 212 (2016) 941-949.
- [192] G. Sun, J. Liu, X. Zhang, X. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, *Angewandte Chemie*, 126 (2014) 12784-12788.
- [193] N. Choudhary, C. Li, H.-S. Chung, J. Moore, J. Thomas, Y. Jung, *ACS nano*, 10 (2016) 10726-10735.
- [194] M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, *Advanced materials*, 26 (2014) 992-1005.
- [195] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum, *ACS nano*, 6 (2012) 1322-1331.
- [196] B. Anasori, M.R. Lukatskaya, Y. Gogotsi, *Nature Reviews Materials*, 2 (2017) 16098.

- [197] O. Mashtalir, M. Naguib, V.N. Mochalin, Y. Dall'Agnese, M. Heon, M.W. Barsoum, Y. Gogotsi, *Nature communications*, 4 (2013) 1716.
- [198] S. Kajiyama, L. Szabova, K. Sodeyama, H. Iinuma, R. Morita, K. Gotoh, Y. Tateyama, M. Okubo, A. Yamada, *ACS nano*, 10 (2016) 3334-3341.
- [199] M.R. Lukatskaya, O. Mashtalir, C.E. Ren, Y. Dall'Agnese, P. Rozier, P.L. Taberna, M. Naguib, P. Simon, M.W. Barsoum, Y. Gogotsi, *Science*, 341 (2013) 1502-1505.
- [200] J. Come, M. Naguib, P. Rozier, M. Barsoum, Y. Gogotsi, P.L. Taberna, M. Morcrette, P. Simon, *Journal of The Electrochemical Society*, 159 (2012) A1368-A1373.
- [201] M. Ghidui, M.R. Lukatskaya, M.Q. Zhao, Y. Gogotsi, M.W. Barsoum, *Nature*, 516 (2014) 78.
- [202] Q. Tang, Z. Zhou, P. Shen, *Journal of the American Chemical Society*, 134 (2012) 16909-16916.
- [203] S. Murali, N. Quarles, L.L. Zhang, J.R. Potts, Z. Tan, Y. Lu, Y. Zhu, R.S. Ruoff, *Nano Energy*, 2 (2013) 764-768.
- [204] S. Xu, G. Wei, J. Li, W. Han, Y. Gogotsi, *Journal of Materials Chemistry A*, 5 (2017) 17442-17451.
- [205] H. Li, Y. Hou, F. Wang, M.R. Lohe, X. Zhuang, L. Niu, X. Feng, *Advanced Energy Materials*, 7 (2017) 1601847.
- [206] J. Yan, C.E. Ren, K. Maleski, C.B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva, Y. Gogotsi, *Advanced Functional Materials*, 27 (2017) 1701264.
- [207] Y. Dall'Agnese, P. Rozier, P.L. Taberna, Y. Gogotsi, P. Simon, *Journal of Power Sources*, 306 (2016) 510-515.

- [208] M.Q. Zhao, C.E. Ren, Z. Ling, M.R. Lukatskaya, C. Zhang, K.L. Van Aken, M.W. Barsoum, Y. Gogotsi, *Advanced materials*, 27 (2015) 339-345.
- [209] M. Zhu, Y. Huang, Q. Deng, J. Zhou, Z. Pei, Q. Xue, Y. Huang, Z. Wang, H. Li, Q. Huang, *Advanced Energy Materials*, 6 (2016) 1600969.
- [210] R.B. Rakhi, B. Ahmed, D. Anjum, H.N. Alshareef, *ACS applied materials & interfaces*, 8 (2016) 18806-18814.
- [211] Y. Tian, C. Yang, W. Que, X. Liu, X. Yin, L.B. Kong, *Journal of Power Sources*, 359 (2017) 332-339.
- [212] Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian, F. Wei, *Advanced materials*, 22 (2010) 3723-3728.
- [213] D. Yu, E. Nagelli, F. Du, L. Dai, *The journal of physical chemistry letters*, 1 (2010) 2165-2173.
- [214] Y. Luo, Y. Zhang, Y. Zhao, X. Fang, J. Ren, W. Weng, Y. Jiang, H. Sun, B. Wang, X. Cheng, H. Peng, *J. Mater. Chem. A*, 3 (2015) 17553-17557.
- [215] H. Guo, M.H. Yeh, Y.C. Lai, Y. Zi, C. Wu, Z. Wen, C. Hu, Z.L. Wang, *ACS nano*, 10 (2016) 10580-10588.
- [216] S.L. Kim, H.T. Lin, C. Yu, *Advanced Energy Materials*, 6 (2016) 1600546.
- [217] X. Tian, J. Jin, S. Yuan, C.K. Chua, S.B. Tor, K. Zhou, *Advanced Energy Materials*, (2017) 1700127.
- [218] F. Zhang, M. Wei, V.V. Viswanathan, B. Swart, Y. Shao, G. Wu, C. Zhou, *Nano Energy*, (2017), <https://doi.org/10.1016/j.nanoen.2017.08.037>.

Graphical abstract

Taking graphene, transition metal dichalcogenides and MXenes as examples, this review summarizes the representative approaches to construct two dimensional nanomaterials-based flexible electrodes with high performance for supercapacitors; and illustrates the structure-property relationships.